In situ control of Si(100) and Ge(100) surface preparation for the heteroepitaxy of III-V solar cell architectures

Sebastian Brückner, Oliver Supplie, Enrique Barrigón, Anja Dobrich, Johannes Luczak et al.

Citation: AIP Conf. Proc. **1477**, 32 (2012); doi: 10.1063/1.4753827
View online: http://dx.doi.org/10.1063/1.4753827
View Table of Contents: http://proceedings.aip.org/dbt/dbt.jsp?KEY=APCPCS&Volume=1477&Issue=1
Published by the American Institute of Physics.

In Situ Control Of Si(100) And Ge(100) Surface Preparation For The Heteroepitaxy Of III-V Solar Cell Architectures

Sebastian Brückner[1,2], Oliver Supplie[1], Enrique Barrigón[3], Anja Dobrich[1], Johannes Luczak[1], Claas Löbbel[1], Ignacio Rey-Stolle[3], Peter Kleinschmidt[1,4], Henning Döscher[1,2] and Thomas Hannappel[1,2,4]

[1] *Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, 14109 Berlin, Germany*
[2] *Technische Universität Ilmenau, Institut für Physik, Postfach 10 05 65, 98684 Ilmenau, Germany*
[3] *Instituto de Energía Solar, Universidad Politécnica de Madrid, Avda. Complutense s/n, 28040 Madrid, Spain*
[4] *CiS Forschungsinstitut für Mikrosensorik und Photovoltaik GmbH, Konrad-Zuse-Straße 14, 99099 Erfurt, Germany*

Abstract. Si(100) and Ge(100) substrates essential for subsequent III-V integration were studied in the hydrogen ambient of a metalorganic vapor phase epitaxy reactor. Reflectance anisotropy spectroscopy (RAS) enabled us to distinguish characteristic configurations of vicinal Si(100) in situ: covered with oxide, cleaned by thermal removing in H_2, and terminated with monohydrides when cooling in H_2 ambient. RAS measurements during cooling in H_2 ambient after the oxide removal process revealed a transition from the clean to the monohydride terminated Si(100) surface dependent on process temperature. For vicinal Ge(100) we observed a characteristic RA spectrum after annealing and cooling in H_2 ambient. According to results from X-ray photo electron spectroscopy and Fourier-transform infrared spectroscopy the spectrum corresponds to the monohydride terminated Ge(100) surface.

Keywords: MOVPE, Si(100), Ge(100), monohydride termination, III-V on Si(100)/Ge(100), H_2 ambient, reflection anisotropy spectroscopy.
PACS: 81.15.Gh, 88.40.jp,78.68.+m, 78.30.Am, 81.05.Cy

INTRODUCTION

The technological interest in the opto-electronic properties of III-V based solar cells drives research for their heteroepitaxial integration on substrates such as Si(100) or Ge(100). An important requirement to achieve low defect densities in the III-V epilayers is a suitable surface preparation of the group IV(100) substrate since structural and chemical properties of surfaces are essential for subsequent heteroepitaxy. Nowadays, triple junction solar cells based on Ge(100) present efficiencies close to 42%. Despite this outstanding results, the microscopic III-V/Ge(100) nucleation and its interface formation has not been fully understood so far. In order to further reduce the cost of multijunction solar cells, the Ge(100) substrate could be replaced by Si(100) where the surface preparation prior to heteroepitaxy is likewise crucial.

MOVPE processing of Si(100) and Ge(100) usually begins with thermal substrate annealing under hydrogen flow for oxide removal. Temperatures over 950°C are sufficient to prepare contamination free Si(100) in MOVPE ambient [1]. After cooling in H_2 ambient the Si(100) surface is covered completely by monohydrides according to FTIR and STM measurement [2]. Detailed STM investigations showed that monohydride termination impedes formation of double layer steps [3], however, Ref [4] reports about double layer step formation on low offcut Si(100) substrates. This contradiction might be related to the interaction of the hydrogen ambient with the Si(100) surface. On the other hand, very little is known about the surface preparation of Ge(100) in H_2 ambient, since the process gas ambient limits the direct access to surface analysis for MOVPE prepared samples.

Reflection anisotropy spectroscopy (RAS) enables in situ characterization of substrate surfaces during MOVPE processing [5]. RA spectra of clean and monohydride terminated Si(100) surfaces are reported in [6]. In [7] and [8] RA spectra of the clean prepared Ge(100) surface with 4° and 6° offcut in [011] is presented, respectively.

In this paper, we show the sensitivity of in situ RAS to monohydride terminations of both Si(100) and Ge(100). The established RA spectra of hydrogen terminated Si(100) [2,8] allowed us to study the interaction of the Si surface with the H_2 process gas dependent on temperature in situ in detail. We also present a characteristic RA spectrum of MOVPE prepared vicinal Ge(100) which differs from UHV studies and which we assign to the monohydride terminated surface. Oxide and carbon removal from the Ge(100) surfaces was confirmed by XPS, while FTIR showed the presence of a monohydride termination after processing in H_2.

8th International Conference on Concentrating Photovoltaic Systems
AIP Conf. Proc. 1477, 32-35 (2012); doi: 10.1063/1.4753827

EXPERIMENTAL

The preparation was carried out in a commercially available MOVPE reactor (Aixtron AIX200) especially modified for surface characterization. An optical view port at the reactor allowed in situ monitoring of the sample surface by RAS (LayTec EpiRAS 200). A dedicated sample transfer system involving a mobile UHV chamber enabled contamination-free access to several surface analysis systems [10] such as LEED (Specs ErLEED 100-A), STM (Specs Aarhus 150), or XPS (Specs Focus 500 and Phoibos 100).

The Si(100) substrates with a misorientation of 6° towards the [011] direction were prepared by annealing at 1000°C for 30 min at 950mbar in purified H_2 process gas as described in Ref [2]. We used Ge(100) substrates with a misorientation of 6° towards the [011] direction specified as "epiready" (supplier: AXT) and specific samples (CrysTec) for FTIR [11]. Without any additional wet chemical pre-cleaning, thermal oxide removal (Fig. 1) was conducted by annealing at 1000 K for 20 min in purified H_2 at a pressure of 100 mbar in a cleaned (liner, susceptor) MOVPE reactor to avoid unintentional contaminations.

RESULTS AND DISCUSSION

Figure 1 shows typical in situ RA spectra of vicinal Si(100) samples measured during the surface preparation in MOVPE: The initially thin SiO_2 layer which covers the substrate [9] exhibits no optical anisotropy (upper panel, grey line). The oxide layer is removed during annealing in pure molecular hydrogen at pressure of 950 mbar at 1250 K and the characteristic RA spectrum of clean vicinal Si(100) develops (upper panel, blue line) showing a broad minimum around 3 eV and a shoulder at 3.4 eV and a small peak at 4.2 eV. After cooling to ambient temperature in H_2 process gas the in situ RA spectrum (Fig. 1, middle panel, orange line) contains two sharp peak structures in a derivative like arrangement around the E_1 and E_2 critical point energies at 3.4 eV and 4.3 eV, respectively. The spectrum agrees well to the characteristic RA spectrum of monohydride terminated vicinal Si(100). [6] FTIR, LEED, and STM measurements confirmed a complete monohydride termination of the Si samples [2]. Also, a strong majority surface reconstruction domain was demonstrated by a (2x1) LEED pattern and STM images showing mostly D_B type double layer steps in [9].

The measurements in Fig. 1 demonstrate the ability to distinguish between the clean and monohydride terminated surfaces of vicinal Si(100) during VPE preparation by in situ RAS. At 1250 K the surface appears to be hydrogen free, while a monohydride termination is measured at 300 K. We performed in situ RAS during stepwise cooling (Fig. 1 lower panel) to reveal the transformation of the line shape in detail: after thermal deoxidation at 1270 K, we constantly observed the broad minimum structure (blue line) associated with a clean surface. During gradual reduction of the temperature (100 K steps) the RAS signal changed (thin grey lines) to a narrower shape (thick orange line) which agrees well with the complete monohydride termination [2] at 300 K as shown in Fig. 1 (middle panel). The transformation is reversible by reheating of the sample. Since the spectra shown in Fig. 1 (lower panel) remained stable over time, they represent characteristic equilibrium conditions for the applied process ambient and respective temperature.

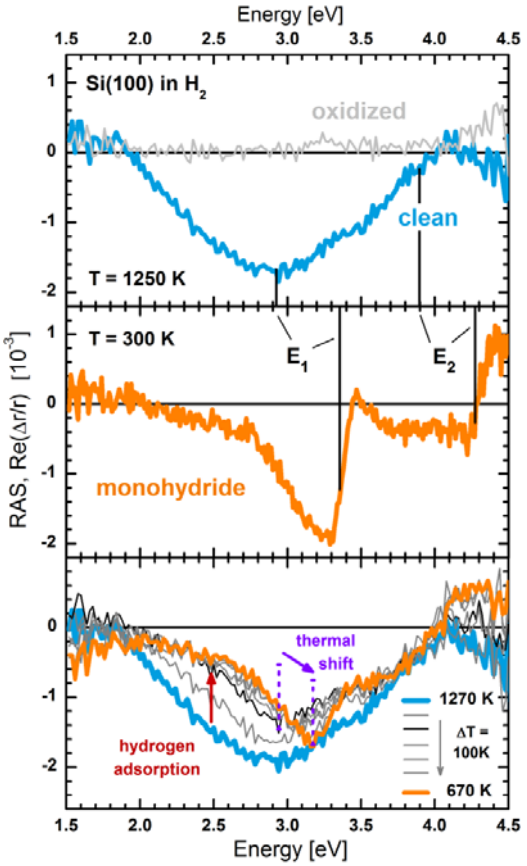

FIGURE 1. RA spectra of vicinal Si(100) measured in situ before (top, grey line), during (top, blue line) and after (middle, orange line) annealing in H_2 ambient. Vertical lines indicate the critical interband transitions of Si [12]. Bottom: RA spectra measured continously during cooling in H_2 after annealing. Arrows indicate different influences on the RA spectra.

Two major trends superimpose in the in situ RA spectra in Fig. 1 (lower panel): sharpening and shifting of the features to blue due to decreasing temperature (small arrows) [13] and characteristic changing due to formation of monohydride bonds (large arrow) [6]. Starting with the broad RAS

feature assigned to clean vicinal Si(100) at 1270 K crucial changes already occurred around 1070 K. From that temperature the spectrum basically consists of a sharp feature which matches with the derivative like shape of the monohydride surface.

From the results shown in Fig. 1 we suggest a monohydride termination of vicinal Si(100) in the hydrogen-based MOVPE process ambient for annealing temperatures below 1000 K. The in situ observations most probably represent the dynamic balance of hydrogen adsorption and desorption events in dependence of the respective process conditions since UHV investigations [14] showed significant desorption from monohydride terminated Si(100) at 800 K and even below. A simple model for temperature dependent hydrogen coverage of Si(100) based on STM observations in UHV [15] agreed very well with the in situ result [9] shown in Fig. 1 (lower panel). For increasing annealing temperature, desorption eventually outbalances adsorption of hydrogen, but partial hydrogen coverage is predicted far beyond 1300 K.

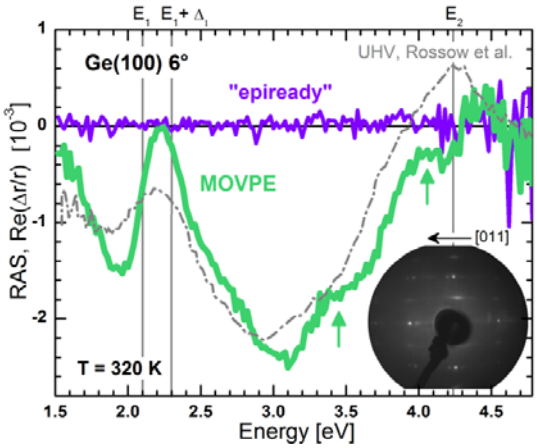

FIGURE 2. RA spectra of vicinal Ge(100) measured at ambient temperature before (violet line) and after (green line) H_2 annealing compared to UHV-prepared, clean vicinal Ge(100) (dash-dotted line) [8]. Vertical lines indicate the critical interband transistions of Ge [12]. Green arrows indicate shoulders evolving in the RA spectrum of the H_2 annealed sample whose LEED pattern (inset) were measured at 168eV after contamination-free transfer to UHV.

In Figure 2 we present RA spectra of "epiready" and H_2 annealed vicinal Ge(100) measured in the MOVPE reactor at 320 K (after cooling in H_2 ambient) as well as the RA spectrum of clean vicinal Ge(100) prepared in UHV [8] for comparison. Due to the amorphous oxide layer the "epiready" surface exhibits a featureless spectrum..

After H_2 annealing the RAS signal of the Ge(100) surface (Fig. 2, green line) consists of a broad minimum around 3 eV and a narrow one at 1.9 eV as well as local maxima around the critical point (CP) energies of Ge(100) (E_1 and $E_1 + \Delta_1$ at about 2.2 eV and E_2 at 4.3 eV, respectively).

The MOVPE prepared sample roughly agrees in the general RAS features with the RAS signal of clean Ge(100) prepared by annealing in UHV [8]. However, the local maximum around 2.2 eV is more pronounced and the minimum around 3 eV is shifted slightly towards higher energies. Further, an additional fine structure around 3.4 eV and 4.0 eV in the RAS signal is observed (arrows in Fig. 3).

In general, shape and amplitude of RA spectra of (100) surfaces depend on the atomic order of the surface regarding cleanliness, surface reconstruction, domain ratio, and chemical configuration [16]. The RAS signal decays linearly if it originates from the surface reconstruction, since signals from mutually perpendicular reconstruction domains cancel each other [17]. The signal intensity is also affected by the impurity concentration on the surface [7]. In contrast, the line shape of the RAS signal may be changed by formation of a monohydride termination when hydrogen saturates the dangling bonds [11] as observed for vicinal Si(100) [6].

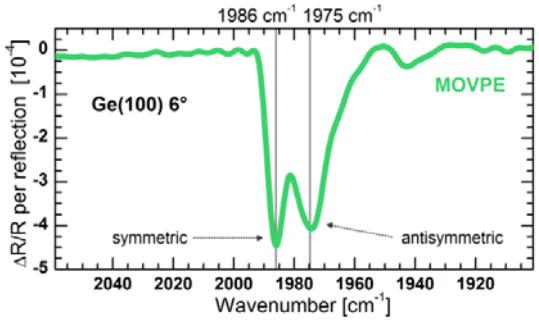

FIGURE 3. FTIR spectrum of MOVPE-prepared vicinal Ge(100) after contamination-free transfer to UHV. The characteristic absorption lines correspond to the symmetric resp. antisymmetric coupled Ge-H stretch modes [11].

We applied several surface sensitive UHV based techniques to analyze the surface properties of the MOVPE prepared Ge sample. According to XPS analysis [18] H_2 annealing of the "epiready" Ge(100) substrates at 1000 K leads to removal of all contaminations such as oxygen and carbon from the surface. The LEED pattern of the deoxidized Ge(100) surface (Fig. 2 inset) shows pronounced spot splitting along [011]. The half-order spots in [011] direction indicate dimer formation on the surface and a clear prevalence of the domain with dimers parallel to the step edge, which corresponds to a preference for D_B-type double layer steps in consistence with vicinal Ge(100) surfaces prepared in UHV [19]. Since dimerization occurs on both clean and monohydride Ge(100) surfaces our LEED pattern does not distinguish between these terminations.

Figure 3 shows ATR mode FTIR measurements after annealing and cooling in H_2 ambient to check

for hydrogen termination. The two characteristic absorption lines at about 1986 and 1975 cm–1 match to coupled Ge–H stretch modes [11]. Hydrogen saturates the residual dangling bonds of the reconstructed Ge(100) and forms H–Ge–Ge–H dimers. Their antisymmetric and symmetric vibrational modes induce dipoles within and perpendicular to the surface plane, respectively.

According to our results from XPS, LEED and FTIR our samples are free of any contamination and terminated with monohydrides after annealing and cooling in H2 ambient. Hence, we assume that both the more pronounced signal shape between 1.8 eV and 2.3 eV and the additional fine structure beyond 3 eV are characteristic of the monohydride Ge(100) surface. We exspect further evidence for the sensitivity of RAS to monohydride termination on the Ge(100) surface by thermal hydrogen desorption under flow of alternative process gases such as N_2 or Ar [9].

CONCLUSION

We demonstrated in situ access to the interaction of both Si(100) and Ge(100) surface with hydrogen ambient. According to the in situ RA spectra the vicinal Si(100) surface is hydrogen free at deoxidation temperatures of 1250K, but a monohydride termination is formed for temperatures below 1000K. H_2 annealing leads to removal of oxides and carbon from vicinal Ge(100) surfaces. ATR mode FTIR spectroscopy confirmed a monohydride termination. In situ RA spectra of H_2 annealed vicinal Ge(100) surfaces showed characteristic deviations from UHV reference data of clean Ge(100). In particular, we assigned the more pronounced features between 1.8 eV and 2.3 eV as well as the additional fine structure beyond 3.0 eV to the monohydride termination.

ACKNOWLEDGMENTS

This work was supported by the BMBF (Project 03SF0329C). E. Barrigón was supported by the Spanish Ministerio de Ciencia e Innovación (TEC2008-01226, TEC2009-11143) and by the Comunidad de Madrid (S2099/ENE1477) and the Consejo Social of the UPM.

REFERENCES

1. H. Döscher, S. Brückner, A. Dobrich, C. Höhn, P. Kleinschmidt, and T. Hannappel, *J. Cryst. Growth* 315, 10 (2011).
2. H. Döscher, A. Dobrich, S. Brückner, P. Kleinschmidt, and T. Hannappel, *Appl. Phys. Lett*. 97, 151905 (2010).
3. A. R. Laracuente and L. J. Whitman, *Surf. Sci*. 545, 70 (2003).
4. B. Kunert, I. Nemeth, S. Reinhard, K. Volz, and W. Stolz, *Thin Solid Films* 517, 140 (2008).
5. J. T. Zettler, *Prog. Cryst. Growth Charact. Mater.* 35, 27 (1997).
6. R. Shioda and J. van der Weide, *Appl. Surf. Sci.* 130–132, 266 (1998).
7. T. Yasuda, L. Mantese, U. Rossow and D.E. Aspnes, *Phys. Rev. Lett.* 74, 3431 (1995).
8. U. Rossow, L. Mantese, and D. E. Aspnes, *J. Vac. Sci. Technol. B* 18, 2229 (2000).
9. S. Brückner, Henning Döscher, Peter Kleinschmidt, and Thomas Hannappel, *Appl. Phys. Lett.* 98, 211909 (2011).
10. T. Hannappel, S. Visbeck, L. Toben, and F. Willig, *Rev. Sci. Instrum.* 75, 1297 (2004).
11. Y. J. Chabal, *Surf. Sci*. 168, 594 (1986).
12. P. Lautenschlager, M. Garriga, L. Vina, and M. Cardona, *Phys Rev B* 36, 4821 (1987).
13. R. J. Cole, S. Tanaka, P. Gerber, J. R. Power, T. Farrell, and P. Weightman, *Phys. Rev. B* 54, 13444 (1996).
14. P. Gupta, V. L. Colvin, and S. M. George, *Phys. Rev. B* 37, 8234 (1988).
15. T. Komeda and Y. Kumagai, *Phys. Rev. B* 58, 1385 (1998).
16. H. Döscher and T. Hannappel, *J. Appl. Phys*. 107, 123523 (2010).
17. N. Witkowski, R. Coustel, O. Pluchery, and Y. Borensztein, *Surf. Sci.* 600, 5142 (2006)
18. S. Brückner, E. Barrigón, O. Supplie, P. Kleinschmidt, A. Dobrich, C. Löbbel, I. Rey-Stolle, H. Döscher, and T. Hannappel, *Phys. Status Solidi RRL* 6, 178–180 (2012)
19. J. E. Griffith et al., *J. Vac. Sci. Technol. A* 6, 493 (1988).